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TITLE UNTANGLING THE WATER GAS SHIFT FROM FISCHER-TROPSCH: A GORDIAN KNOT?

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UNTANGLING THE WATER GAS SHIFT FROM FISCHER-TROPSCH: A GORDIAN KNOT?

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ABSTRACT

The water gas shift reaction is an integral part of the Fischer-Tropsch synthesis. Although it may appear convenient to consider the water gas shift a separate reaction in some cases, a detailed examination of the mechanism indicates that the water gas shift and other synthesis gas reactions share several elementary reactions. Experimental support for the relevant elementary reactions for the water gas shift on metals, metal oxides, and in homogeneous solution is examined, from both surface and complex chemistry. Multiple paths leading to a net water gas shift reaction may be available; oxygen transfer and reaction through C-H-O intermediates may take place.

INTRODUCTION

The water gas shift reaction is catalyzed by numerous metals and oxides. Thus, in any environment containing CO and H_2O, or CO_2 and H_2, the water gas shift reaction,

$$CO + H_2O \rightleftharpoons CO_2 + H_2, \qquad (1)$$

or its reverse, the water gas reaction, may occur. The water gas shift is used to regulate H_2 and CO concentrations in synthesis gas, and it occurs as part of synthesis gas reactions such as the Fischer-Tropsch synthesis, in

which CO and H_2 are starting materials, and CO_2 and H_2O may be products. At typical synthesis gas reaction temperatures, the equilibrium constant for the water gas shift is close enough to unity and the reaction proceeds rapidly enough that all four species can be expected to be present. The economics of synthesis gas reactions usually require that oxygen rejection be via H_2O rather than CO_2; therefore, control of the oxygen-carrying product through the water gas shift may be desirable.

Although the water gas equilibrium is sometimes conceptually separated from other synthesis gas reactions, it probably shares elementary reactions with them and thus cannot be separated either in a theoretical or practical way. This is an important point; if the water gas shift itself is considered an elementary step (which it cannot be in a heterogeneously catalyzed system), its function in a synthesis gas reaction such as Fischer-Tropsch cannot be understood. It is tautological to attribute, for example, the production of H_2O as the oxygen-carrying product for an iron-catalyzed Fischer-Tropsch system to iron's activity in the water gas shift reaction. The differences between H_2O- and CO_2-producing catalysts are rather within some subset of elementary reactions occurring under Fischer-Tropsch conditions to give an effective water gas shift. Identification of these

elementary reactions will allow the design of improved Fischer-Tropsch catalysts.

In the conventional phenomenological approach to catalytic kinetics, a mechanism is found that gives orders of reaction similar to those in the empirical rate equation. The approach I will take in this paper is complementary to the phenomenological approach, but it is seldom used.[1] Studies of elementary reactions will be emphasized in order to provide a basis for suggesting their participation in the water gas shift.

Increasing availability of experimental data and of computer calculational capability makes this approach more useful than it has been in the past. A calculational analysis of the mechanism built up from the elementary reactions is not possible within the scope of this paper, but work is in progress on estimating (or obtaining from the literature) rate constants for elementary reactions of interest and combining them to give overall reaction rates.

The organization followed in this paper will be similar to that in my analysis of the Fischer-Tropsch synthesis.[1] The same notation will be used. However, because the water gas shift reaction takes place with metal, metal oxide, and homogeneous catalysts, those subdivisions will be used. Relevant material will be evidence for intermediates or reactions on (1) the metals in the catalysts used

industrially, and ') other metals. Direct observation of intermediates or reactions will be preferred to inference from kinetics, and systems in which elementary reactions are isolated will be preferred to systems of complex reactions. The literature has been covered from 1960 through mid-1982, with emphasis since 1970.

WATER GAS SHIFT REACTION ON METALS

Metal catalysts are of particular interest for understanding the relation of the water gas shift reaction to the Fischer-Tropsch synthesis, because of the reduced nature of the Fischer-Tropsch catalysts under reaction conditions. The evidence for the relevant elementary reactions has been reviewed.[1] Publications since that time have generally supported those reactions. Deuterium adsorbs dissociatively on Rh(100);[2] potassium on iron surfaces increases the adsorption energy of hydrogen.[3] Adsorption of hydrogen is hindered by adsorbed electronegative atoms, such as oxygen,[4] carbon,[4,5] and nitrogen.[5] Several techniques have given more detail on the adsorption of CO on nickel,[6] alumina-supported cobalt,[7] platinum,[8] copper,[8] and rhodium.[2] The degree of dissociation of CO on rhodium is subject to differing interpretations,[9] and CO is reported to dissociate on stepped nickel surfaces,[10] but not on kinked platinum surfaces.[11] The presence of adsorbed

potassium on platinum strengthens the adsorption of CO,[12] as do sodium, potassium, and cesium on nickel, in addition to inducing CO dissociation.[13] Conversely, an oxygen adlayer on Cu-Ni surface alloys weakens CO adsorption.[14] These effects on CO adsorption are generally interpreted to mean that the alkali metals increase backbonding from the metal to CO, and electronegative elements decrease the backbonding.

A thermal desorption study of CO and H_2O adsorbed on Ru(001) shows that the presence of water induces a strongly-bound state of CO, possibly dissociated.[15] CO_2 dissociates on alumina-supported rhodium to CO and adsorbed O, although the details of this interaction, and the effect of hydrogen on it, are not clear.[16] Coadsorption of CO_2 and H_2 on alumina-supported rhodium gave adsorbed formate, as observed by infrared spectroscopy.[17]

The overall kinetics of the water gas shift reaction have been studied on unsupported iron[18] and platinum,[19] on alumina-supported Group 7B, 8, and 1B metals, some of which were also supported on silica and carbon,[20] on zeolite- and alumina-supported rhodium,[21] and on zeolite-supported ruthenium.[22]

For unsupported iron at high temperatures, an oxygen transfer mechanism,

$$CO_2(g) \rightleftharpoons CO(g) + O(ads) \qquad (2)$$

$$H_2O(g) \rightleftharpoons H_2(g) + O(ads), \qquad (3)$$

was deduced.[18] However, this is in conflict with findings that CO adsorbs readily on metals and H_2 adsorbs dissociatively. (See discussions in Ref. 1, and references therein.) For unsupported platinum, the stoichiometric number method[23] was used to interpret overall kinetics and isotopic labeling experiments. The proposed mechanism[19] is given in Table I. The adsorbed intermediate was not identified.

For supported metals, the situation appears to be more complex. Because the commonly-used supports, such as alumina, can adsorb water significantly and the other components of the water gas shift equilibrium to lesser degrees, the catalyst may be bifunctional, with some processes taking place on the metal surfaces, some on the support surfaces, and some at the interface between the metal and the support. A comparative study[20] of the water gas shift reaction on rhenium, cobalt, iron, nickel, rhodium, ruthenium, palladium, iridium, osmium, platinum, copper, and gold showed activities ranging over three orders of magnitude for the metals supported on alumina. Platinum and rhodium were found to be most active on alumina supports, of intermediate activity on silica, and least active on carbon. A mechanism was proposed for a bifunctional catalyst. This mechanism is given in Table II, where M indicates a site on the metal,

and MO a site on the support. However, the activity of a bifunctional catalyst should be strongly dependent on the dispersion of the metal, and no such dependence was found.

Methane was a significant product in the water gas shift reaction over zeolite- and alumina-supported rhodium, and both methane and ethane were observed in small amounts over the alumina-supported catalyst.[21] The activity of alumina alone for the reaction was two orders of magnitude less than for the alumina-supported rhodium. Zeolite-supported ruthenium also produced methane in addition to the water gas shift reaction, but the support seems to have less effect than for rhodium.[22] The occurrence of methanation greatly complicates the interpretation of these results.

A set of elementary reactions describing the water gas shift reaction on most metals is given in Table III. This table includes the reactions of Table X in Ref. 1, with all adsorption-desorption steps made explicit, and nucleophilic attack of adsorbed OH on adsorbed CO added, partly because of more recent studies,[17,20] and partly because of evidence on the homogeneously catalyzed reaction, to be discussed later in this paper. Hydroxycarbonyl is given as the product of nucleophilic attack, rather than formate, because several reactions can be written for formate formation and decomposition, none of which have significant support from surface studies. Although inclusion of formate at this time

would be both speculative and lengthy, it may be justified with further study.

WATER GAS SHIFT REACTION ON OXIDES

The water gas shift catalysts used industrially have been iron and chromium oxides (high-temperature catalyst) and copper, zinc, chromium, and aluminum oxides (low-temperature catalyst). Limited information is available on the adsorption of H_2, H_2O, CO, and CO_2 on these oxides. However, many of the elementary steps of the water gas shift are adsorption-related: adsorption and dissociation, or their reverse, association and desorption.

H_2 Adsorption

At least three, and as many as seven types of hydrogen have been identified as adsorbed species on zinc oxide.[24-32] Infrared spectroscopy has identified three species: a heterolytically dissociated species, Zn-H and OH on adjacent sites, that appears to be active in hydrogenations;[24-27] a low-temperature molecularly adsorbed species that participates in H_2-D_2 exchange;[28,29] and a species inactive for hydrogenation that appears to be bridged, Zn-H-Zn or O-H-O.[26] Temperature-programmed desorption (TPD) studies and conductivity studies seem to indicate the presence of greater numbers of hydrogen species,[30-32] but

these have not all been identified with infrared species. At least two TPD peaks appear to represent different reaction paths to desorption for the species identified in the infrared studies.[33]

Although zinc oxide is considered the hydrogen activation component in methanol and water gas shift catalysts, other components of the catalysts can also adsorb hydrogen. TPD results[34] show five different types of hydrogen adsorbed on gamma-alumina between -196 and 450 C. Chromia and chromia-silica adsorb hydrogen, although to a lesser extent than zinc oxide. A very low-temperature form of hydrogen adsorbed on chromia appears to be molecular, analogous to the low-temperature form on zinc oxide.[35] A heterolytic dissociative adsorption of hydrogen is reported at intermediate temperatures, and transformation of the Cr^{3+} bonded to H to Cr^{2+} and OH is reported to take place at higher temperatures.[36]

The reactions producing the various forms of hydrogen adsorbed on oxides are likely to be

$$H_2 + MO \rightleftharpoons MO\text{-}H_2(\text{physisorbed}) \qquad (4)$$

$$MO\text{-}H_2(\text{physisorbed}) \rightleftharpoons H\text{-}MO\text{-}H \qquad (5)$$

$$H\text{-}MO\text{-}H + 2\ MO \rightleftharpoons OM\text{-}H\text{-}MO\text{-}H\text{-}OM. \qquad (6)$$

Other routes are possible, and diffusion on the surface may be important, as indicated by the TPD results. Reactions 4-6 account in a simple way for relationships among the three

species observed by infrared spectroscopy, but the reactions themselves have not been observed directly.

H_2O Adsorption

The adsorption of water onto metal oxides gives hydroxyl groups, intermediates also formed by the adsorption of hydrogen. In the case of water, dissociation is to a hydrogen that adds to an oxide oxygen and a hydroxyl that adds to a metal ion. Hydrogen bonding with the oxide oxygens and hydroxyl groups also causes molecular adsorption of water.

On iron oxide, adsorption isotherms[37], dielectric relaxation,[38] infrared spectroscopy,[39] and ultraviolet photoemission spectroscopy[40] have shown both molecularly adsorbed and dissociated water. Water is physisorbed onto surface hydroxyls. Physisorbed water was observed by infrared spectroscopy on an iron-chromium catalyst; dissociative chemisorption was also deduced.[41]

Water adsorption on zinc oxide has been studied by adsorption isotherms[42] and a combination of thermogravimetry and infrared spectroscopy;[43] again, molecular adsorption and dissociation were both observed. Water adsorbs dissociatively onto oxygen-treated copper and zinc,[44] although it adsorbs poorly onto clean copper and zinc surfaces. For a low-temperature shift catalyst, both hydroxyls and undissociated water have been observed by infrared spectroscopy.[45]

Dissociation increases with the degree of reduction of the catalyst. Molecularly adsorbed water appears to be present on both catalyst and support.

On alumina, as determined by microcalorimetry and infrared spectroscopy,[46] water is physisorbed, then molecularly chemisorbed and dissociated. Silica[47] and chromia[48] behave similarly. The processes of water adsorption on silica-alumina appear to be similar to those on silica and alumina, but the combination has a greater capacity for water adsorption than what would be extrapolated by a linear combination of the two.[49]

The reactions of water adsorption on oxides can be summarized:

$$H_2O + MO \rightleftharpoons H_2O\text{-}MO(\text{physisorbed}) \quad (7)$$

$$H_2O\text{-}MO(\text{physisorbed}) \rightleftharpoons H_2O\text{-}MO \quad (8)$$

$$H_2O\text{-}MO(\text{physisorbed}) \rightleftharpoons MO\text{-}HOH \quad (9)$$

$$H_2O\text{-}MO \rightleftharpoons HO\text{-}MO\text{-}H \quad (10)$$

$$MO\text{-}HOH \rightleftharpoons HO\text{-}MO\text{-}H. \quad (11)$$

There appear to be two kinds of water chemisorbed molecularly: one in which the oxygen is bonded to the metal ion (reaction 8), and one in which the water is hydrogen bonded to the oxygen or hydroxyl groups of the oxide (reaction 9).

CO Adsorption

CO adsorption on oxides has been less studied and therefore is not as well understood as CO adsorption on metals. Infrared spectroscopy has been the method of choice for examining Co adsorption on metal oxides; few other methods have been used. In general, a low-frequency group of bands (1100 to 1800 cm^{-1}) is attributed to carbonate, bicarbonate, formate, and carboxyl or hydroxycarbonyl, and a higher-frequency group of bands (2000 to 2250 cm^{-1}) is attributed to a weakly adsorbed species, in which the carbon is sigma-bonded to the metal ion with no backbonding or the interaction is primarily electrostatic. Carbonyl bands (1900 to 2000 cm^{-1}) are sometimes observed. Interpretation of some of the bands is not unambiguous. Harrison and Thornton[50] have concluded that the weakly bonded CO is adsorbed, carbon down, perpendicular to the surface, as in carbonyls, but the bonding is primarily electrostatic. Copper is an exception to this, in that significant pi bonding appears to be present, and this model is not completely consistent with other data, suggesting the possibility of some pi bonding for other metals. Infrared absorption frequencies for CO adsorbed on transition-metal ions on silica[51] appear to be consistent with this model, and a simple correlation between heat of adsorption and CO frequencies for several oxides[52] also argues for a simple bonding model. The C-O bond for

this type of CO adsorption is strengthened relative to its gas-phase value.

Conductivity data suggest a partly cationic CO adsorbed on the Fe^{2+} ions of Fe_2O_3,[53] although the charge of the CO changes from partially positive to partially negative with increasing reduction of the oxide.[54] CO was adsorbed onto a reduced iron-chromium catalyst with apparent formation of carbonates and carbonyls;[41] however, one of the bands attributed to a carbonyl (2095 cm^{-1}) is in the range usually considered to belong to a weakly-bound species. On FeO, CO appears to be adsorbed at a metal ion, although the ultraviolet photoelectron spectrum cannot be fully interpreted.[55] With potassium on FeO, the CO is adsorbed more strongly, probably as a carbonyl.[55]

Adsorption on copper oxide gives a weakly bound species,[56,57] carbonyls,[56-62] and carbonates, bicarbonates, and formates;[56,58,59] in addition, if another component, such as alumina, silica, or other metal oxide, is present, bicarbonate and formate concentrations will be increased. A large range of frequencies is observed for carbonyls (2000-2200 cm^{-1}); apparently differences in the preparation of the catalyst affect the relative amounts of copper in the three oxidation states. It has not been possible to relate frequencies unambiguously to oxidation states because of the lack of appropriate model compounds. Copper carbonyls that

may simulate surface compounds have been synthesized only recently.[63]

Zinc oxide shows bands in the weakly bound region[61,64-66] and the carbonate region[64-66], but none that have been identified as carbonyls. Other surface diagnostics tend to confirm these identifications.[67] Angle-resolved photoelectron spectroscopy shows the CO to be adsorbed, carbon end down, on the zinc .oms.[68]

Both pure and supported chromia show bands indicating a weakly adsorbed species,[48,69-73] a carbonyl,[71] and carbonates.[69,72,73] Transient response techniques have given results consistent with these interpretations.[74] However, for a copper chromite catalyst, it was concluded that carbonyls formed only on copper.[56]

Alumina is reported to form one[69,75] or two[76] weakly adsorbed species and carbonates. Kinetic data support the presence of two types of adsorption, but these cannot be correlated readily with those identified by infrared spectroscopy.[77] A potassium promoter on alumina results in carboxylate and carbonate upon adsorption of CO and CO_2.[78]

Adsorption of CO on silica is not observed at temperatures above 75 C.[58]

Magnesia forms a weakly adsorbed species and carbonates,[59,79] and there is some evidence for a species

containing an unpaired electron. This species has been identified as a carbonyl radical[80] or a polymeric radical anion.[81] These species participate in the disproportionation of CO, forming carbonates and carbon. A similar species is formed on calcium and strontium oxides.[82]

The probable reactions representing CO adsorption on metal oxides, are then

$$CO + MO \rightleftharpoons OM\text{-}CO(physisorbed) \qquad (12)$$

$$OM\text{-}CO(physisorbed) \rightleftharpoons OM\text{-}CO \qquad (13)$$

$$CO + MOMO \rightleftharpoons M_2CO_3 \qquad (14)$$

Distinctions will not be made here between unidentate and bidentate species. The formation of bicarbonates and formates from CO must involve interactions with hydrogen or hydroxide and will be discussed later. The stoichiometries and structures of the polymeric radical anions formed on alkaline earth oxides are not known, so reactions cannot be written for their formation and eventual disproportionation to carbonates and carbon. Therefore, these reactions will be neglected at this time, but they should be considered for catalysts containing the alkaline earth metals.

CO_2 Adsorption

Carbon dioxide initially physisorbs on metal oxide surfaces and then chemisorbs in three ways: with the carbon bonded to metal to give a carboxyl group, with an oxygen

bonded to metal, or with the carbon bonded to oxygen to give a carbonate. Relatively little evidence exists, however, for the M-OCO species.

Fe_2O_3 adsorbs CO_2 to give a weakly adsorbed species and possible carbonates, bicarbonates, and carboxyls.[83,84] Chromia and chromia-silica give species similar to those on Fe_2O_3.[69,85]

Copper oxide adsorbs CO_2 weakly,[58] with possible formation of carbonates and carboxyls.[86] Zinc oxide forms carbonates and a carboxyl upon CO_2 adsorption.[64,83,87] The carboxyl group probably does not carry a full negative charge.[67]

Two weakly adsorbed species have been identified on silica by infrared spectroscopy,[88] but this observation is in contradiction to the observation of carboxyl groups on silica exposed to CO_2 by electron spin resonance[89] and adsorption-desorption techniques.[90]

On alumina, carbonates and bicarbonates[69,91-96] and one,[91] two,[92] or three[93] weakly bonded species have been observed. No carboxyls have been reported. An adsorption isotherm study generally supports the carbonate identifications.[97] The species and their relative concentrations are strongly influenced by heat treatment and the crystal structure of the alumina.[94]

On magnesia, carbonates are formed,[79b,92b,95] and a weakly-bound species has been observed.[79b]

Soluble CO_2 complexes of cobalt and alkali metal cations have been characterized.[98] The carbon is bonded to the cobalt, and the oxygens to the alkali metal cations. The infrared C-O frequencies are in the range of those observed for carboxyls on surfaces.

The reactions for adsorption of CO_2 on metal oxides can be summarized:

$$CO_2 + MO \rightleftharpoons MO\text{-}CO_2(\text{physisorbed}) \quad (15)$$

$$MO\text{-}CO_2(\text{physisorbed}) \rightleftharpoons OM\text{-}CO_2 \quad (16)$$

$$MO\text{-}CO_2(\text{physisorbed}) \rightleftharpoons MO\text{-}CO_2 \quad (17)$$

$$MO\text{-}CO_2(\text{physisorbed}) \rightleftharpoons OM\text{-}OCO. \quad (18)$$

Interactions Among Adsorbed Species

The major interactions appear to take place among adsorbed species, rather than between adsorbed and gas-phase species. However, information about these steps is incomplete and sometimes contradictory.

The presence of hydroxyl groups on the surface of several of these oxides appears to promote CO_2 adsorption, although this effect has not been studied in detail. Water interacts with adsorbed CO_2 on magnesia to produce bicarbonate.[99] This could come about by nucleophilic attack on the carbon by hydroxyl,

$$OM\text{-}OCO + OM\text{-}OH \rightleftharpoons OM\text{-}OC(O)OH + MO, \quad (19)$$

hydrogen transfer,

$$MO\text{-}CO_2 + OM\text{-}OH \rightleftharpoons MO\text{-}C(O)OH + OM\text{-}O, \quad (20)$$

or oxygen insertion,

$$OM\text{-}CO_2 + OM\text{-}OH \rightleftharpoons OM\text{-}OC(O)OH + MO. \quad (21)$$

In a relevant solution reaction, Cu^{2+} has been found to catalyze the nucleophilic attack of water at a carbonyl carbon.[100]

CO and H_2O, and CO_2 and H_2, have been coadsorbed on zinc and magnesium oxides and the surface intermediates observed by infrared spectroscopy.[101] Formate ions were the predominant species observed. Formate,[102,103] acetyl and acetate,[102] and carbonate and bicarbonate[103] intermediates have been trapped during $CO\text{-}H_2$ and $CO_2\text{-}H_2$ reactions on copper-zinc catalysts. Water and CO adsorbed on an iron-chromium catalyst interact to produce formate.[41] A possible reaction producing formate is

$$OM\text{-}CO + OM\text{-}OH \rightleftharpoons OM\text{-}OC(H)O. \quad (22)$$

This is an oxygen insertion into the M-C bond (or carbon migration to oxygen) with hydrogen transfer. It may be broken down into

$$OM\text{-}CO + OM\text{-}OH \rightleftharpoons OM\text{-}C(O)OH + MO \quad (23)$$

$$OM\text{-}C(O)OH \rightleftharpoons OM\text{-}OCOH \quad (24)$$

$$OM\text{-}OCOH \rightleftharpoons OM\text{-}OC(H)O. \quad (25)$$

Hydrogen addition to adsorbed CO_2 will also give formate:

$$M\text{-}OCO + M\text{-}H \rightleftharpoons M\text{-}OC(H)O + M. \quad (26)$$

Both lattice and adsorbed oxygen may oxidize CO to CO_2 on copper oxide[104,105] and Fe_2O_3.[53] On chromia, adsorbed CO and oxygen react to give carbonates and carboxyls.[106,107] The weakly bonded CO with an infrared absorption at 2187 cm^{-1} appears to be the reactive species.[106] Coadsorption of CO with oxygen on hydrated magnesia produces infrared absorptions in the carbonate region and no absorptions characteristic of adsorbed CO.[79b] This reaction may be

$$OM\text{-}CO + OM\text{-}O \rightleftharpoons OM\text{-}CO_2 + MO \quad (27)$$

$$OM\text{-}CO_2 + OM\text{-}O \rightleftharpoons OM\text{-}OCO_2 + MO. \quad (28)$$

The interaction between adsorbed CO and hydrogen on zinc oxide has been investigated by several groups.[108-113] The evidence is consistent with inductive strengthening of the bonds between the adsorbed species and the zinc oxide, with no new chemical bonds formed.[113] These species may be more reactive than the individually adsorbed species; otherwise, this interaction is more relevant to methanation and methanol formation.

Overall Reaction Studies

Studies of the overall water gas shift reaction over iron, copper, and cobalt-molybdenum catalysts have been reviewed recently.[114] Empirical rate equations are

summarized there and will not be considered here, although some conclusions on elementary steps in the mechanism will be reconsidered in the light of the independent evidence for the elementary reactions. The cobalt-molybdenum catalysts will not be considered here because less information exists for elementary reactions on those catalysts, and their sulfidation may introduce significant differences into the mechanism of reaction.

For the iron-chromium catalysts, two mechanisms have been proposed. The regenerative mechanism[115] involves oxygen transfer through adsorbed oxygen atoms; this essentially consists of reactions 2 and 3 or may also include the adsorption of the other reactants. Most of the evidence for this mechanism has been obtained at higher temperatures than are of industrial interest for the water gas shift reaction, and it may be primarily of interest in metallurgy.[18,116,117] Mechanisms proceeding through a C-H-O intermediate, such as the formate ion, have also been proposed.[118]

For the copper-zinc catalysts, most of the overall studies[119,120] conclude that an intermediate, probably a formate,[120] is important in the mechanism. The single dissenting opinion[121] is based mainly on theoretical considerations and fails to explain several points. A comparison of formate decomposition on zinc and magnesium oxides with the

water gas shift reaction led to the conclusion that formate is an important intermediate.[101]

A combined kinetic and infrared study of the water gas shift reaction on alumina[122] showed that formate ion exists on the working catalyst and that some formate ions may not participate in the overall reaction. Infrared spectroscopy suggests that carbonate is not an important intermediate. Little if any carboxyl was observed.

Although the evidence for most of the steps is poor in terms of observed intermediates or elementary reactions, a mechanism for the water gas shift on oxide catalysts is summarized in Table IV.

HOMOGENEOUS WATER GAS SHIFT REACTION

It is not yet clear to what degree reactions observed in homogeneous metal complexes can be assumed to occur in heterogeneous systems. However, mechanisms for the water gas shift reaction have been worked out for several homogeneous systems, and some of the elementary steps appear to be similar to those in heterogeneous systems.

Mononuclear and polynuclear carbonyls of several transition metals catalyze the water gas shift. In acidic solution, catalysis by rhodium,[123] ruthenium,[124] and palladium[125] complexes has been observed, and in basic solution, by iron,[126-130] nickel,[131]

ruthenium,[128,129,131-133] rhodium,[134-136] osmium,[137] iridium,[128,137] platinum,[138,139] and chromium, molybdenum, and tungsten complexes.[126,132]

Notation can obscure the similarities between the homogeneous and heterogeneous reactions. Therefore, in this discussion reactions will be written in the notation used for the metal surfaces [illegible]ds that do not participate in the reaction will be omitted. Table V summarizes the elementary reactions suggested for the homogeneous water gas shift reaction. Reactions for both the acidic and basic media are included.

In proposing a general mechanism for the homogeneous water gas shift reaction, I will not consider charges on metal complexes. Many of the reactions take place with both neutral and charged complexes (Table V), and this simplification makes clearer the relationship to surface reactions. However, the charges will affect the energetics of the reactions and must be taken into account in calculations of specific systems.

Nucleophilic attack of hydroxide or water at a carbonyl carbon has been well documented:[140]

$$M\text{-}CO + OH \rightleftharpoons M\text{-}C(O)OH \qquad (29)$$

$$M\text{-}CO + H_2O \rightleftharpoons H\text{-}M\text{-}C(O)OH. \qquad (30)$$

The metallocarboxylic acids can break down to give CO_2:[141]

$$M\text{-}C(O)OH \rightleftharpoons M\text{-}H + CO_2. \quad (31)$$

CO_2 can also react with metal complexes to give formates:[142]

$$CO_2 + M\text{-}H \rightleftharpoons M\text{-}OC(H)O. \quad (32)$$

The equilibrium

$$CO + OH^- \rightleftharpoons HCO_2^- \quad (33)$$

also gives formate, which can complex with a metal:

$$M + HCO_2^- \rightleftharpoons M\text{-}OC(H)O^-. \quad (34)$$

Molybdenum hexacarbonyl reacts with formate ion to give a formatomolybdate complex and a carboylate complex.[143] Photochemical enhancement of formate decomposition by group 6B metal hexacarbonyls[144] appears to support dissociation of CO from a carbonyl, followed by formate complexation and decomposition, as steps in the reaction. Both monodentate formate[145] and metallocarboxylic acids[141] may be intermediates, yielding CO_2 and H_2 upon decomposition, but the metallocarboxylic acid pathway may be energetically more favorable, at least in the case of iron.[145]

Dissociation of H_2O and formation of H_2,

$$H_2O + M \rightleftharpoons H\text{-}M\text{-}OH \quad (35)$$

$$H\text{-}M\text{-}H \rightleftharpoons M + H_2, \quad (36)$$

are known. Addition of water to rhodium[146] and palladium[147] complexes followed by elimination of hydrogen has been observed. Another relevant reaction is the photochemical substitution of water for CO in $Re_2(CO)_{10}$; the

substitution proceeds through a somewhat indirect mechanism, however, with photochemical homolysis of the Re-Re bond as the first step.[148] Under further irradiation, the water ligand dissociates to give $HRe(CO)_5$ and $Re_4(CO)_{12}(OH)_4$.

The addition of CO to an unsaturated metal complex or its substitution for hydrogen are both likely:

$$CO + M \rightleftharpoons M\text{-}CO \qquad (37)$$

$$H\text{-}M\text{-}H + CO \rightleftharpoons M\text{-}CO + H_2 \qquad (38)$$

$$M\text{-}H + CO \rightleftharpoons M\text{-}CO + H. \qquad (39)$$

The water gas shift reaction has also been photocatalyzed with a ruthenium complex, apparently because of photoinitiation by CO dissociation from the complex.[149]

The bicarbonate equilibrium should also be included:

$$CO_2 + OH^- \rightleftharpoons HCO_3^-. \qquad (40)$$

CO_2 can be disproportionated to CO and carbonate by transition metal dianions,[150] in a reaction that may be a part of some of the homogeneously catalyzed water gas shift and suggests some aspects of the heterogeneous reaction.

A zeolite catalyst prepared from ruthenium hexamine appears to operate through a similar mechanism. Ruthenium hexamine exchanged into zeolites shows activity for the water gas shift from 90 C to 230 C.[151] Intermediates identified by infrared spectroscopy suggest a mechanism involving

nucleophilic attack by water on CO coordinated to ruthenium to give a rutheniumcarboxylic acid.

COMPARISON OF MECHANISMS FOR DIFFERENT CONDITIONS

It should be emphasized for the following discussions that the evidence for most of the elementary reactions is incomplete. The reactions on metal surfaces, particularly CO_2 and H_2O association-dissociation, are the best supported. Many fewer studies are available for adsorption on oxides, owing to the difficulties of preparing well-characterized oxide surfaces. The adsorption-desorption reactions are fairly well established, but questions remain as to the nature of the species formed by CO and CO_2 adsorption on oxides. The steps in which the intermediate is formed and decomposed are the least supported for all mechanisms. It is not clear to what degree formate, hydroxycarboxyl, or oxygen transfer contribute to the overall reaction, although most of the evidence points to the participation of an H-C-O intermediate for the lower-temperature processes.

Considerable similarity exists among the mechanisms proposed here and previously for the water gas shift on metals, metal oxides, and in homogeneous solutions. Adsorption and desorption steps on the surfaces are similar, with the exception of physisorption, to the association reactions in

solution. In all three mechanisms, H_2 dissociates to atoms, and H_2O dissociates to hydrogen and hydroxyl. Although the reactions may be similar for CO and CO_2 adsorption, the adsorbed species on metals and oxides may have significantly different reactivities from each other and from complexed CO and CO_2 in solution. For CO on metals, backbonding weakens the C-O bond; for most oxides, backbonding is absent or almost so, and the C-O bond is strengthened relative to the gas-phase molecule. However, products of apparent nucleophilic attack on carbon are observed in all media. CO oxidation by adsorbed oxygen atoms on metals is the reverse of CO_2 dissociation. This reaction also appears likely on oxides, but less so in solution. However, it has been observed in one homogeneous system.[152]

Reactions forming a C-H-O intermediate have not been observed directly on surfaces. Formic acid or a formate ion adsorbed as $M\text{-}O_2CH$ is an attractive intermediate because of the stoichiometry of formic acid and its known surface reactions:

$$HCOOH \rightleftharpoons H_2 + CO_2 \qquad (41)$$

$$HCOOH \rightleftharpoons H_2O + CO. \qquad (42)$$

However, the formation of adsorbed formate from CO adsorbed carbon and down requires several elementary steps of reaction with hydroxyl and rearrangement (reactions 23-25), or

reaction with oxygen and hydrogen atoms. None of these reactions have been observed. Formation from CO_2 would involve only a hydrogen transfer (reaction 26). Again, this has not been observed in heterogeneous systems. A large volume of literature, which cannot be reviewed within the scope of this paper, deals with the decomposition of formic acid on metal and metal oxide surfaces. A survey of some of the more recent of this literature shows great differences, apparently depending on the method of observation as well as the substrate. For example, most static methods show that the hydroxyl hydrogen is abstracted by metals and oxides to give surface formates,[153] but a dynamic study shows that a hydroxycarbonyl radical is formed by the abstraction of the carbon-bonded hydrogen by the metal surface and that the radical can detach from the surface.[154] Formation of an anhydride intermediate has been proposed,[155] and an anhydride has been observed by infrared reflectance spectroscopy.[156] However, the lack of such an observation in the H_2-H_2O-CO-CO_2 systems suggests that this is an unlikely pathway for the water gas shift reaction. A beta-hydride elimination has been suggested as the decomposition route from a formidorhodium complex to CO_2 and the hydrido complex.[157] Formic acid has also been suggested as an intermediate in the water gas shift on the basis of its overall kinetics of decomposition on a low-temperature shift

catalyst.[120] However, supporting evidence in the form of observed elementary reactions would be highly desirable.

A simpler set of elementary reactions (reactions 29-31) can be written for the CO-hydroxycarbonyl-CO_2 transformation, but few hydroxycarbonyl or carboxyl intermedates have been observed on surfaces. The observation that iron hydroxycarbonyl complexes decompose more rapidly than formido complexes[145] suggests that they may be the kinetically more important intermediates; their short lifetimes and consequently low steady-state concentrations may prevent their observation. On the other hand, they may be too unstable to form on surfaces.

Some of the products appear not to play a part in the water gas shift reaction except to remove a small amount of material from the system. Carbonates and the inactive form of hydrogen on oxides are in this category.

THE WATER GAS SHIFT AND THE FISCHER-TROPSCH SYNTHESIS

The water gas shift reaction is simpler than the Fischer-Tropsch synthesis. It commonly achieves equilibrium, whereas Fischer-Tropsch is at least partly controlled by kinetics. It can be represented by a conventional balanced chemical reaction, whereas Fischer-Tropsch must be represented by a generalized chemical reaction, or a collection of chemical reactions. All this points to the

probability that the water gas shift can be represented by a smaller set of elementary reactions than Fischer-Tropsch. A set of elementary reactions has been proposed for the mechanism of the Fischer-Tropsch synthesis,[1] and sets of elementary reactions have been proposed here for the mechanisms of the water gas shift reaction on metals, on oxides, and in homogeneous solution. In this section, the relationships between these two groups of elementary reactions will be examined.

Publications since the proposal of the mechanism for the Fischer-Tropsch synthesis give no reason to alter that set of elementary reactions. Adsorption of H_2 and CO on transition metals, both pure and modified with promoters and poisons, has been reviewed.[158] A statistical analysis to evaluate correlations between H_2 and CO dissociation and other properties of metals has also been carried out.[159] H_2 dissociation was found to correlate with heat of vaporization, heat of fusion, molar heat capacity, Debye temperature, atomic volume, electronegativity, first and second ionization energies, and electrical conductance. CO dissociation was found to correlate with heat of fusion, molar heat capacity, electrical conductance, and electronegativity. Several of these parameters are related to the metal-metal bond energy, and the others may relate to electronic effects.

Although attempts to observe formyl intermediates on rhodium surfaces failed,[160] increasing numbers of formyl metal complexes are being synthesized.[161] The protonation route for hydrogenation has been further supported.[162] Several methods of C-C bond formation have been demonstrated in complexes.[163] The reverse of C-H bond formation, the oxidative addition of hydrocarbons to iridium complexes, has been demonstrated.[164] Gas-phase studies of interactions between metal atoms and hydrocarbons[165] should give information such as bond energies that can be used in estimating rate constants for these reactions, and are showing some differences between the interactions of different metal atoms with hydrocarbons. The acidity of metal hydrides[166] is another set of information that will be useful in evaluating mechanisms, particularly in solution, and possibly in extrapolation to surfaces. Reactions of interest are being studied in early transition metal complexes[167] and actinide complexes,[168] but these reactions are stoichiometric rather than catalytic. Relevant organometallic reactions have been reviewed.[169]

Several kinetic studies support the participation of carbon atoms and partially hydrogenated carbon as intermediates.[170] From observations of this type, it has been suggested that hydrogenolysis can be regarded as a reverse Fischer-Tropsch synthesis.[171] Oxidation and carburization

of iron have been further studied, and it appears that some iron oxide may be present under synthesis conditions.[172] Changes in kinetic regimes were observed in methanation over nickel foils[173] and in the production of hydrocarbons and oxygenates over $LaRhO_3$.[174] Where Schulz-Flory analysis has been applied to product distributions, both consistent[175,176] and inconsistent[170a,173,176,177] distributions have been observed. Product distributions have been modeled for situations other than the simple Flory model, some of which are more selective.[175,178]

Of closer relevance to the water gas shift are the nucleophilic activation of CO to reduction by hydrogen,[179] analogous to the nucleophilic attack by water or hydroxide proposed for the water gas shift. Coadsorption of CO and H_2 on iron[180] and ruthenium[181] leads to lessened dissociation for both. Most likely, the reaction of water with surface carbon to give methane[182] and the interactions among surface carbon, CO, and CO_2[183] are relevant to both the water gas shift and Fischer-Tropsch. However, more information is needed on the elementary reactions.

Two of the components of the water gas equilibrium, CO and H_2, are the starting materials for the Fischer-Tropsch synthesis. The other two, CO_2 and H_2O, are products of the synthesis. However, the Fischer-Tropsch reactants are on opposite sides of the water gas equilibrium, as are the

products. Thus, the water gas shift can help or hinder the Fischer-Tropsch synthesis by altering the concentrations of reactants and products.

Since the two processes have these components in common, adsorption and desorption reactions must be shared, as must the dissociation reactions of H_2, H_2O, and CO_2. Aside from these reactions, there appear to be no further overlaps between the water gas shift and Fischer-Tropsch. The dissociation of CO appears not to be a part of the water gas shift. Hydroxycarbonyl may be an intermediate in acid or ester formation in Fischer-Tropsch, but evidence here is very limited. Also, if formate intermediates, which have been observed under Fischer-Tropsch conditions, are hydrogenated significantly, some of these reactions may overlap.

If the overlaps between the water gas shift and Fischer-Tropsch are limited to adsorption-desorption and association--dissociation reactions, then consideration of modifications to Fischer-Tropsch catalysts to provide oxygen rejection by H_2O rather than CO_2 may be relatively simple. Catalysts on which the H_2O association and desorption reactions are favored over the CO_2 association and desorption reactions will give a water product. Unfortunately, data for these reactions is not available for a wide range of metals.

Further applications of the relation between the water gas shift and Fischer-Tropsch are in understanding the

Kölbel-Englehardt synthesis and CO_2 methanation. The differences here are not in the elementary reactions, but in the relative concentrations of reactants and intermediates, which may give rise to different paths by effectively reducing the rate of one path to zero, while making significant another path that is inactive in the water gas shift or Fischer-Tropsch.

The overlap, hoever, of the association-dissociation and adsorption-desorption reactions between the water gas shift and Fischer-Tropsch means that it is not useful to separate these two processes conceptually. The water gas shift, although a simpler set of elementary reactions than Fischer-Tropsch, cannot itself be regarded as an elementary reaction. An attempt at a mathematical separation of the kinetics of the water gas shift from the kinetics of Fischer--Tropsch will give meaningless results because the sets of elementary reactions are not orthogonal. Thus, the shorthand of attributing various effects observed in the Fischer-Tropsch synthesis to the water gas shift should be avoided, and an attempt should be made to attribute the effects to a particular elementary reaction or set of elementary reactions.

METHANOL SYNTHESIS

Although the scope of this paper does not permit a detailed discussion of methanol synthesis, that reaction must be closely related to the water gas shift over the low-temperature catalyst, since the catalysts are similar. An ideal situation would be to be able to write a list of elementary reactions encompassing both methanol synthesis and the water gas shift. However, the intermediates in methanol synthesis have not been unambiguously identified.[184] Clearly the largest difference between the two processes is in the oxidizing power of the reactants: synthesis gas for methanol is more reducing than either side of the water gas equilibrium. However, small amounts of CO_2 promote methanol synthesis. Again, as in the Fischer-Tropsch synthesis, adsorption-desorption of H_2, H_2O, CO, and CO_2 and association-dissociation reactions of H_2, H_2O, and CO_2 are probably common to both processes. The CO that is hydrogenated to methanol remains associated, as is likely for the CO that is oxidized in the water gas shift. As is the case in the water gas shift, it is not clear whether the intermediates in CO hydrogenation are bonded to the catalyst through oxygen (formate-methoxy route) or through carbon (formyl-hydroxymethyl route), or whether both of these routes are significant.[185]

SUMMARY AND OUTLOOK

The water gas shift shares a significant number of elementary reactions with the Fischer-Tropsch synthesis, and probably with the Kölbel-Engelhardt synthesis, CO_2 methanation, and methanol synthesis. Oxygen transfer from CO_2 or H_2O to the catalyst and then to H_2 or CC may be the predominant route at higher temperatures in heterogeneous systems and appears to be possible for homogeneous systems. However, a C-H-O intermediate also participates at lower temperatures, particularly in homogeneous systems. This intermediate may be formate or hydroxycarbonyl, but little information now exists that can clarify whether one or both are important.

More information is needed about the interactions of H_2, H_2O, CO, and CO_2 on well-characterized oxide surfaces. Studies of formic acid as a model compound may also be useful, but caution is necessary in their interpretation. The relationship of homogeneous reactions to heterogeneous catalysis is still not clear, but the parallels in the water gas shift appear to be significant. Again, more studies of the intermediates on surfaces will help to elucidate this relationship.

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TABLE I

Mechanism Proposed by Masuda and Miyahara[19] for Water Gas Shift Reaction on Unsupported Platinum

$CO + M \rightleftharpoons M\text{-}CO$

$H_2O + 2\,M \rightleftharpoons M\text{-}H + M\text{-}OH$

$M\text{-}CO + M\text{-}OH \rightleftharpoons$ adsorbed intermediate

adsorbed intermediate $\rightleftharpoons M\text{-}CO_2 + M\text{-}H$

$M\text{-}CO_2 \rightleftharpoons M + CO_2$

$2\,M\text{-}H \rightleftharpoons 2\,M + H_2$

TABLE II

Mechanism Proposed by Grenoble, Estadt, and Ollis[20]

$H_2O + MO \rightleftharpoons HO\text{-}MO\text{-}H$

$H_2O + MO \rightleftharpoons H_2O\text{-}MO$

$H_2O + 2\ M \rightleftharpoons M\text{-}OH + M\text{-}H$

$CO + M \rightleftharpoons M\text{-}CO$

$M\text{-}CO + H_2O\text{-}MO \rightleftharpoons OM\text{-}O(H)C(H)O$

$OM\text{-}O(H)C(H)O + M \rightleftharpoons M\text{-}O(H)C(H)O$

$M\text{-}O(H)C(H)O \rightleftharpoons M + CO_2 + H_2$

TABLE III

Proposed Mechanism of Water Gas Shift on Metals

$H_2 + M \rightleftharpoons M\text{-}H_2(\text{physisorbed})$

$M\text{-}H_2(\text{physisorbed}) \rightleftharpoons H\text{-}M\text{-}H$

$CO + M \rightleftharpoons M\text{-}CO(\text{physisorbed})$

$M\text{-}CO(\text{physisorbed}) \rightleftharpoons M\text{-}CO$

$H_2O + M \rightleftharpoons M\text{-}H_2O(\text{physisorbed})$

$M\text{-}H_2O(\text{physisorbed}) \rightleftharpoons M\text{-}OH_2$

$CO_2 + M \rightleftharpoons M\text{-}CO_2(\text{physisorbed})$

$M\text{-}CO_2(\text{physisorbed}) \rightleftharpoons M\text{-}CO_2$

$M\text{-}CO \rightleftharpoons M\text{-}\overset{O}{\underset{}{\text{C}}}$

$M\text{-}\overset{O}{\underset{}{\text{C}}} \rightleftharpoons O\text{-}M\text{-}C$

$M\text{-}OH_2 \rightleftharpoons H\text{-}M\text{-}OH$

$M\text{-}OH \rightleftharpoons H\text{-}M\text{-}O$

$M\text{-}CO + M\text{-}O \rightleftharpoons M\text{-}CO_2$

$M\text{-} \quad + M\text{-}OH \rightleftharpoons M\text{-}C(O)OH$

$M\text{-}C(O)OH \rightleftharpoons H\text{-}M\text{-}CO_2$

TABLE IV

Proposed Mechanism for the Water Gas Shift Reaction on Metal Oxides

Reaction	Number
$H_2 + MO \rightleftharpoons MO\text{-}H_2(physisorbed)$	(4)
$MO\text{-}H_2(physisorbed) \rightleftharpoons H\text{-}MO\text{-}H$	(5)
$H\text{-}MO\text{-}H + 2\ MO \rightleftharpoons OM\text{-}H\text{-}MO\text{-}H\text{-}OM$	(6)
$H_2O + MO \rightleftharpoons H_2O\text{-}MO(physisorbed)$	(7)
$H_2O\text{-}MO(physisorbed) \rightleftharpoons H_2O\text{-}MO$	(8)
$H_2O\text{-}MO(physisorbed) \rightleftharpoons MO\text{-}HOH$	(9)
$H_2O\text{-}MO \rightleftharpoons HO\text{-}MO\text{-}H$	(10)
$MO\text{-}HOH \rightleftharpoons HO\text{-}MO\text{-}H$	(11)
$CO + MO \rightleftharpoons OM\text{-}CO(physisorbed)$	(12)
$OM\text{-}CO(physisorbed) \rightleftharpoons OM\text{-}CO$	(13)
$CO + MOMO \rightleftharpoons M_2CO_3$	(14)
$CO_2 + MO \rightleftharpoons MO\text{-}CO_2(physisorbed)$	(15)
$MO\text{-}CO_2(physisorbed) \rightleftharpoons OM\text{-}CO_2$	(16)
$MO\text{-}CO_2(physisorbed) \rightleftharpoons MO\text{-}CO_2$	(17)
$MO\text{-}CO_2(physisorbed) \rightleftharpoons OM\text{-}OCO$	(18)
$OM\text{-}OCO + OM\text{-}OH \rightleftharpoons OM\text{-}OC(O)OH + MO$	(19)
$MO\text{-}CO_2 + OM\text{-}OH \rightleftharpoons MO\text{-}C(O)OH + OM\text{-}O$	(20)
$OM\text{-}CO_2 + OM\text{-}OH \rightleftharpoons OM\text{-}OC(O)OH + MO$	(21)
$OM\text{-}CO + OM\text{-}OH \rightleftharpoons OM\text{-}C(O)OH + MO$	(23)
$OM\text{-}C(O)H \rightleftharpoons OM\text{-}OCOH$	(24)

TABLE IV (continued)

Reaction	Number
$OM\text{-}OCOH \rightleftharpoons OM\text{-}OC(H)O$	(25)
$M\text{-}OCO + M\text{-}H \rightleftharpoons M\text{-}OC(H)O + M$	(26)
$OM\text{-}CO + OM\text{-}O \rightleftharpoons OM\text{-}CO_2 + MO$	(27)
$OM\text{-}CO_2 + OM\text{-}O \rightleftharpoons OM\text{-}OCO_2 + MO$	(28)

TABLE V

Previously Proposed Elementary Reactions

for Homogeneous Water Gas Shift Reaction

Reaction	Reference
$M\text{-}CO + OH^- \rightleftharpoons M\text{-}C(O)OH^-$	126,128,130,131
$M\text{-}CO + OH^- \rightleftharpoons M\text{-}H + CO_2$	137
$M\text{-}CO + OH^- \rightleftharpoons M\text{-}H^- + CO_2$	133
$[M\text{-}CO]OH \rightleftharpoons M\text{-}C(O)OH$	138
$M\text{-}CO + H_2O \rightleftharpoons H\text{-}M\text{-}C(O)OH$	128,131
$M\text{-}CO + Me_3N \rightleftharpoons M\text{-}C(O)NMe_3$	132
$M\text{-}C(O)NMe_3 + H_2O \rightleftharpoons M\text{-}H^- + CO_2 + Me_3NH^+$	132
$M\text{-}CO^+ + H_2O \rightleftharpoons H\text{-}M\text{-}C(O)OH^+$	129
$M\text{-}C(O)OH \rightleftharpoons M\text{-}H + CO_2$	128,131,138
$H\text{-}M\text{-}C(O)OH \rightleftharpoons M + HC(O)OH$	138
$M\text{-}C(O)OH^- + H_2O \rightleftharpoons H\text{-}M\text{-}C(O)OH + OH^-$	128,131
$M\text{-}C(O)OH^- \rightleftharpoons M\text{-}H^- + CO_2$	126
$M\text{-}C(O)OH^- + B \rightleftharpoons M\text{-}C(O)O^{2-} + BH^+$	130
$M\text{-}C(O)O^{2-} + H_2O \rightleftharpoons M\text{-}H^- + HCO_3^-$	130
$M\text{-}(Cl)C(O)OH^+ \rightleftharpoons M^+ + CO_2 + H^+ + Cl^-$	129
$M\text{-}OC(H)O \rightleftharpoons M\text{-}H + CO_2$	138
$M\text{-}OC(H)O^- \rightleftharpoons M\text{-}H^- + CO_2$	124,126,132
$H\text{-}M\text{-}H \rightleftharpoons M + H_2$	124,126,128,131, 132,136,137,138
$H\text{-}M\text{-}H + CO \rightleftharpoons M\text{-}CO + H_2$	128,131,136

TABLE V (continued)

Reaction	Reference
$M\text{-}H^- + CO \rightleftharpoons M\text{-}CO + H^-$	126,133
$M\text{-}H^- + H_2O \rightleftharpoons M + H_2 + OH^-$	133
$M + CO \rightleftharpoons M\text{-}CO$	125,126,128,131, 132,136,137
$M^+ + CO \rightleftharpoons M\text{-}CO^+$	129
$M^- + CO \rightleftharpoons M\text{-}CO^-$	133
$M + H_2O \rightleftharpoons H\text{-}M\text{-}OH$	136,138
$M^- + H_2O \rightleftharpoons M\text{-}H + OH^-$	125,126,132,137
$M + HC(O)OH \rightleftharpoons H\text{-}M\text{-}OC(H)O$	138
$M + HCOO^- \rightleftharpoons M\text{-}OC(O)H^-$	125,126,132
$H\text{-}M\text{-}OH + S \rightleftharpoons [H\text{-}M\text{-}S]OH$	136,138
$[H\text{-}M\text{-}S]OH + CO \rightleftharpoons [H\text{-}M\text{-}CO]OH + S$	136,138
$CO + OH^- \rightleftharpoons HCO_2^-$	126,128,131,132
$CO_2 + OH^- \rightleftharpoons HCO_3^-$	128,131
$HCO_2^- + H_2O \rightleftharpoons H_2 + CO_2 + OH^-$	128,131
$H^- + H_2O \rightleftharpoons H_2 + OH^-$	126,133

TABLE VI

Proposed Mechanism for the Homogeneous

Water Gas Shift Reaction

Reaction	Number
$M\text{-}CO + OH \rightleftharpoons M\text{-}C(O)OH$	(29)
$M\text{-}CO + H_2O \rightleftharpoons H\text{-}M\text{-}C(O)OH$	(30)
$M\text{-}C(O)OH \rightleftharpoons M\text{-}H + CO_2$	(31)
$CO_2 + M\text{-}H \rightleftharpoons M\text{-}OC(H)O$	(32)
$CO + OH^- \rightleftharpoons HCO_2^-$	(33)
$M + HCO_2^- \rightleftharpoons M\text{-}OC(H)O^-$	(34)
$H_2O + M \rightleftharpoons H\text{-}M\text{-}OH$	(35)
$H\text{-}M\text{-}H \rightleftharpoons M + H_2$	(36)
$CO + M \rightleftharpoons M\text{-}CO$	(37)
$H\text{-}M\text{-}H + CO \rightleftharpoons M\text{-}CO + H_2$	(38)
$M\text{-}H + CO \rightleftharpoons M\text{-}CO + H$	(39)